



# Catalytic wet oxidation of organic compounds over N-doped carbon nanotubes in batch and continuous operation



Diogo F.M. Santos, Olívia S.G.P. Soares, Adrián M.T. Silva, José L. Figueiredo,  
Manuel Fernando R. Pereira\*

Laboratory of Separation and Reaction Engineering—Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto,  
4200-465 Porto, Portugal

## ARTICLE INFO

### Article history:

Received 26 March 2016  
Received in revised form 14 June 2016  
Accepted 18 June 2016  
Available online 19 June 2016

### Keywords:

Carbon nanotubes (CNTs)  
Catalytic wet oxidation (CWO)  
Phenol  
Continuous operation

## ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were treated by ball milling with and without a nitrogen precursor (melamine) to introduce nitrogen functionalities. These materials were tested as catalysts in batch and continuous catalytic wet oxidation (CWO) experiments for the degradation of phenol in aqueous solution. The influence of several reaction parameters (temperature, dissolved oxygen concentration and initial phenol concentration) were studied in both operating modes. Temperature had a more significant effect on the reaction rate than the dissolved oxygen concentration, an optimal temperature of 160 °C being determined. The experiments with different initial phenol concentrations showed that higher amounts of phenol and carbon contents were removed when the initial concentration of phenol was increased. MWCNTs with N-groups showed high catalytic activity for phenol removal in both operation modes, as also observed when performing some experiments with oxalic acid. For instance, complete phenol degradation and 50% of total organic carbon (TOC) removal were achieved after 2 h in batch operation at 160 °C and 6 bar of oxygen partial pressure with the N-doped catalyst (against 68% and 50%, respectively, with the undoped sample). In the continuous mode reactor, 80% and 50% of phenol and TOC removals were observed at the steady state with the N-doped catalyst, in this case at 160 °C and 12 bar of oxygen partial pressure with an initial phenol concentration of 500 mg L<sup>-1</sup>. A significant regeneration of the N-doped catalyst was achieved by thermal treatment at 600 °C under nitrogen atmosphere.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Water is one of the most precious natural resources in the planet since it is necessary for the survival of humans, animals and plants. With the population and industrial growth, large amounts of wastewaters are produced which need proper treatment before being discharged into the aquatic environment. The increasing amounts of highly recalcitrant and bio-toxic organic pollutants render infeasible the traditional treatment options, such as physical separation and biological treatments [1]. Catalytic wet oxidation (CWO) is one of the solutions to remove bio-refractory organic pollutants from industrial wastewaters when they have a very high carbon content [2]. In this process, the organic compounds are oxidized into intermediate products, or mineralized into CO<sub>2</sub> and H<sub>2</sub>O [3], in the presence of a catalyst, typically at temperatures between 130 and 250 °C and pressures between 10 and 50 bar [4].

Several noble metal based catalysts (Pt, Pd, Ru, Ir Rh, Rd, etc.) [5–11] and metal oxide catalysts (FeO<sub>3</sub>, CoO, MnO, MnO<sub>2</sub>, ZnO, CuO, etc.) [5,11–14] have demonstrated good activity for the oxidation of organic compounds by CWO. However, the cost of noble metals and the typical deactivation observed due to the deposition of carbonaceous materials (poisoning) and/or leaching of the active phase [7,8,15,16], which also pollutes the treated effluent, are some of the limitations towards the implementation of the CWO process. In this context, recent works have mainly focused on the development of an active but also stable and cheap catalyst for CWO.

Carbon materials, such as activated carbons [17–24], carbon xerogels [18,25,26] and carbon nanotubes (CNTs) [1,3,27–31] have already been successfully used as catalysts for the CWO of organic compounds. In particular, the application of CNTs as catalyst is interesting due to their thermal and mechanical properties, and non-microporous nature (minimizing mass transfer resistances) [32,33]. The production of CNTs is also increasingly cheaper due to the optimization of the production processes. The catalytic activity of these materials is related to their chemical and textural properties, which can be optimized with different treatments [28,31].

\* Corresponding author.

E-mail address: [fpereira@fe.up.pt](mailto:fpereira@fe.up.pt) (M.F.R. Pereira).

Most of the works published so far concluded that basic surface groups are the most beneficial for the reaction [1,27,28], while others described a positive influence of surface carboxylic acid groups [3,29–31]. The positive role of S-containing groups has also been reported [28,34].

The most common basic surface groups are N-containing groups, which can be introduced into the carbon surface by different treatments. Recently, the use of materials enriched with nitrogen has attracted particular interest. One of the first publications in this domain, for the treatment of water pollutants by CWO, deals with carbon materials prepared from foams and fibers enriched with nitrogen, in this particular case for degradation of aniline [35]. Rocha et al. [27] produced several samples of CNTs with different types and amounts of functional groups, using chemical and thermal treatments. It was reported that after oxidation with nitric acid, the O-containing surface groups increased significantly, increasing also the acidity of the materials while decreasing their catalytic activity for degradation of oxalic acid by CWO. The thermal treatments removed selectively the O-containing surface groups from the CNTs, leading to an increase of the basicity and to an improvement of their catalytic activity. Restivo et al. [34] performed chemical and thermal treatments to CNTs, and tested them in the oxidation of oxalic acid and phenol by CWO and ozonation processes. After the treatment with urea and thermal treatment at 200 °C, the catalytic activity was significantly improved. The authors ascribed this improvement to the incorporation of nitrogen groups. Recently, a novel solvent-free methodology was reported [36] to incorporate N-functionalities into CNTs by ball milling followed by a thermal treatment, and very high catalytic activities were achieved when these metal-free catalysts were tested in batch mode for the removal of oxalic acid by CWO [37].

In most cases, the CWO experiments using carbon materials as catalysts are performed in batch mode. With only a small number of papers showing tests in continuous mode, mostly using activated carbon as catalyst [20–22,38–40]. Eftaxias et al. [38] studied the CWO of phenol over activated carbon in a trickle bed reactor. Nearly complete phenol conversion (from an initial concentration of 5000 mg L<sup>-1</sup>) was obtained at 160 °C, 2 bar of oxygen partial pressure (P/O<sub>2</sub>) and a liquid space time of 0.4 h using between 6.6 and 7.0 g of catalyst. Suárez-Ojeda et al. [22] investigated the influence of temperature and oxygen partial pressure on the continuous CWO of phenol, *o*-cresol and 2-chlorophenol, also employing activated carbon as catalyst. These authors showed that the conversion of pollutants, the total organic carbon (TOC) abatement and the chemical oxygen demand (COD) removal were highly influenced by the temperature, almost independent of the pressure (in the range studied), and that the catalyst stability was sensitive to both temperature and pressure. Stüber et al. [39] compared the CWO of phenol in a slurry reactor and in a trickle bed reactor. The initial rates of phenol oxidation were much higher in the slurry reactor when compared to the trickle bed reactor. The authors mentioned mass transfer limitations, ineffective catalyst wetting and preferential flow as possible explanations for these results. Since different phenomena can affect the observed reaction rates when the reaction is performed in a batch or in a continuous reactor, running the experiments in both types of reactor is important to understand the reaction mechanisms and to select the most appropriate catalyst and operating conditions to enable a viable application of the technology.

In the present work, undoped and N-doped CNTs prepared by ball milling were tested as catalysts for the CWO of phenol in batch and continuous reactors. Catalyst doping with nitrogen was performed in order to introduce basic surface groups that, as mentioned above, are expected to be beneficial to the reaction. Preliminary runs were carried out in the batch reactor with the different catalysts to find the most promising one. Then, the most active catalyst was tested under different operating conditions,

in batch and in continuous modes, varying different parameters (dissolved oxygen concentration, temperature and initial phenol concentration). The deactivation and regeneration of the N-doped catalyst was also investigated. An experiment in continuous operation under intensified conditions, i.e. using a higher initial phenol concentration, was also performed to assess the efficiency of the catalyst under more realistic conditions.

In this context, batch experiments were mainly performed for catalyst screening, and continuous mode runs to study the catalyst stability and intensified conditions. In both cases, different operating conditions were tested.

## 2. Experimental

### 2.1. Materials

Commercially available multi-walled carbon nanotubes (MWCNTs) were purchased from NANOCYL™ (NC3100 series). According to the supplier, these nanotubes have an average diameter of 9.5 nm, an average length of 1.5 μm and carbon purity higher than 95%. The original MWCNTs, without any additional treatment, are referred as CNT-O. A ball milling treatment was applied to CNT-O in a Retsch MM200 mill without any gas flow, during 4 h with a vibration frequency of 15 vibrations/s, since these operating conditions were already identified as the most appropriate to increase the surface area of MWCNTs, an important parameter in oxidation reactions, as previously reported for ozonation [41]. The resulting material was identified as CNT-BM. The incorporation of N-functionalities was performed using an easy method described in another publication [36]. Briefly, 0.6 g of the original carbon nanotubes was mixed with 0.26 g of N using melamine (Fluka; purity ≥ 99%) as nitrogen precursor. The mixture was ball milled for 4 h with a vibration frequency of 15 vibrations/s. Then, the material was thermally treated at 600 °C during 1 h under nitrogen flow, and this catalyst was identified as CNT-BM-M.

The catalysts CNT-O and CNT-BM-M were also impregnated with platinum (1 wt%), by the incipient wetness impregnation method with a solution of the correspondent salt (H<sub>2</sub>PtCl<sub>6</sub>, purchased from Alfa Aesar). After impregnation, the materials were dried at 100 °C for 24 h and then thermally treated under nitrogen flow at 200 °C for 1 h and reduced at 200 °C under hydrogen flow for 3 h [42]. As reference catalyst, CeO<sub>2</sub> in powder form was prepared by the precipitation method [43], using an aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O.

### 2.2. Catalyst characterization

The textural characterization of the materials was based on the N<sub>2</sub> adsorption isotherms determined at –196 °C with a Quantachrome Nova 4200e apparatus. The nature and amounts of the surface oxygenated groups were determined by temperature programmed desorption (TPD), in an Altamira Instruments AMI-300 apparatus. Thermogravimetric analysis (TGA) was carried out under helium, with a heating rate of 5 °C min<sup>-1</sup> from 50 to 900 °C, in a STA 409 PC/4/H Luxx Netzsch thermal analyser. The pH at the point of zero-charge (pHpzc) was measured by analysis of the pH change of NaCl solutions of different initial pH values when exposed to samples of the prepared materials. The nature and amounts of the N-groups on the surface of the materials were determined by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCALAB 200A spectrometer. Additional details can be found elsewhere [36].

### 2.3. Experimental procedure

Batch CWO experiments were performed in a 160 mL 316-SS high pressure batch reactor housing a glass liner (Parr instruments,

USA Mod. 4564). Regarding the preliminary experiments for catalyst screening, 75 mL of the pollutant solution (90 or 75 mg L<sup>-1</sup> for oxalic acid or phenol, respectively) and 0.2 g of catalyst (i.e. 2.7 g L<sup>-1</sup>) were placed into the reactor. The reactor was flushed with pure nitrogen to ensure the complete removal of oxygen, pressurized with 5 bar of nitrogen and then heated up to the desired temperature (140 or 160 °C for oxalic acid or phenol, respectively) under continuous stirring (500 rpm). When the desired temperature was reached, nitrogen was removed from the reactor and oxygen was introduced until an oxygen partial pressure of 5 bar (in the case of oxalic acid), or air was injected until an oxygen partial pressure of 6 or 8 bar (in the case of phenol). This was considered time zero for the reaction. Slightly different conditions were selected for phenol and oxalic acid taking into account our previous reports [28] dealing with the removal of these pollutants, where it was shown that oxalic acid can be oxidized under less severe conditions than those needed for phenol degradation. The reactions were performed for 2 h, with several liquid samples being collected at different times to determine the evolution of phenol concentration. At the end of the experiments, a liquid sample was also collected to determine the TOC content. After the screening experiments, phenol was selected as model pollutant to study different operating conditions in the batch reactor, because this pollutant is more difficult to oxidize than oxalic acid. The stirring speed was tested at 500 and 700 rpm, the oxygen partial pressure between 6 and 12 bar, the temperature between 120 and 180 °C and the initial phenol concentration between 30 and 75 mg L<sup>-1</sup>, at a catalyst load of 2.7 g L<sup>-1</sup>. The maximum variations obtained for the phenol and TOC removals in repeated experiments were 6 and 3%, respectively.

Continuous CWO experiments were performed in a completely automated tubular reactor from Microactivity PID Eng&Tech equipped with a HPLC pump and a high-pressure liquid-gas separator. The catalysts tested were mixed with an inert material (0.2 g of catalyst and 1.8 g of carborundum), to ensure that the height of the catalyst bed was sufficient to allow a correct reading of the temperature by the thermocouple. The catalysts were supported in glass wool to guarantee that no clogging of the pipes occurred by dragging of the catalyst. The system was pre-heated under nitrogen flow (4 bar of pressure) until the desired temperature (140 or 160 °C for oxalic acid or phenol, respectively). When the desired temperature was reached, nitrogen was replaced by oxygen, the pressure inside the reactor increased to the desired value (5 or 8 bar for oxalic acid or phenol, respectively) and the model pollutant solution fed at 0.25 mL min<sup>-1</sup>. During the experiments, several liquid samples were collected to determine the evolution of the phenol concentration. When the steady state was reached, a liquid sample was also collected to determine the TOC content. Once again, experiments changing the temperature, the oxygen partial pressure and the initial phenol concentration were performed. Additional experiments under intensified conditions were performed with a much higher initial phenol concentration (500 mg L<sup>-1</sup>), a catalyst mass (CNT-O, CNT-BM or CNT-BM-M) of 1.3 g, at 160 °C and with an oxygen partial pressure of 12 bar. Between repetitions of the same experiment, the maximum variation obtained for both phenol and TOC removal was 3%.

#### 2.4. Analytical techniques

Oxalic acid, phenol and the respective by-products were determined by high performance liquid chromatography (HPLC) with a Hitachi Elite LaChrom system equipped with a Diode Array Detector (L-2450). For low molecular weight carboxylic acids, including oxalic acid, an Alltech OA-1000 column (300 mm x 6.5 mm) working at room temperature was used. The mobile phase was a H<sub>2</sub>SO<sub>4</sub> (5 mmol L<sup>-1</sup>) solution with a flow rate of 0.5 mL min<sup>-1</sup>. The

**Table 1**  
Main properties of the catalysts [36].

Catalysts	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	CO (μmol g <sup>-1</sup> )	CO <sub>2</sub> (μmol g <sup>-1</sup> )	N content <sup>a</sup> (wt%)
CNT-O	291	200	23	0
CNT-BM	391	173	44	0
CNT-BM-M	355	338	214	3.65

<sup>a</sup> N content was measured by XPS.

injection volume and the wavelength used were 15 μL and 200 nm, respectively.

For the determination of phenol, 1,4-benzoquinone and hydroquinone, a Purospher Star RP-18 end capped column (250 mm × 4.6 mm) working at room temperature was employed. The mobile phase was a mixture of water and methanol 70/30 (v/v) with a flow rate of 1 mL min<sup>-1</sup>. The quantification of phenol was performed at λ = 270 nm, while the by-products (1,4-benzoquinone and hydroquinone) were quantified at λ = 245 nm and 290 nm, respectively.

The total organic carbon (TOC) content was determined using a Shimadzu TOC-5000A analyser.

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

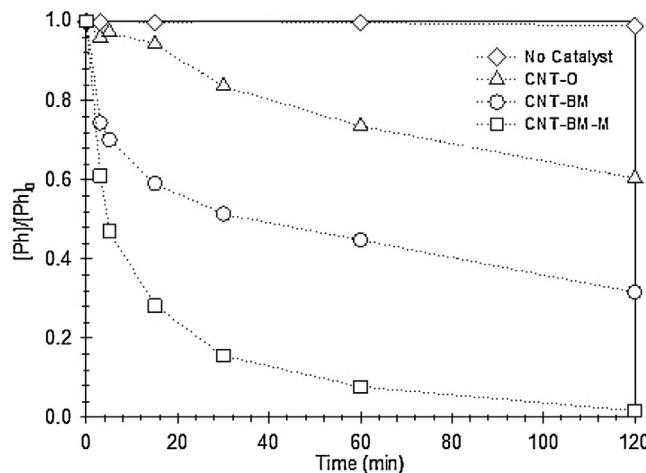
**Table 1** summarizes the main properties of the catalysts used in this work. The detailed characterization of these materials can be found elsewhere [36].

The ball-milling treatment increases significantly S<sub>BET</sub>, from 291 (CNT-O) to 391 m<sup>2</sup> g<sup>-1</sup> (CNT-BM), due to partial disentanglement of the CNTs and breaking of tubes [41]. When melamine is mixed with the original carbon nanotubes, the increase in S<sub>BET</sub> is lower, most likely due to the N-containing functional groups that can block the access of nitrogen to the inner cavities or promote agglomeration of the CNTs [36]. The amounts of CO and CO<sub>2</sub> released by temperature programmed desorption (TPD) of the original (CNT-O) and the ball-milled (CNT-BM) catalysts show that the surface chemistry in terms of O-containing groups is not really affected during the ball milling treatment, as these values are very close. N-doping causes a slight increase in the CO and CO<sub>2</sub> released, which means that a small amount of O-containing functional groups are introduced into the catalyst surface. Since this catalyst is thermally treated at 600 °C, the increase in the CO and CO<sub>2</sub> released is due to the increase in the carbonyl/quinone or ether groups that are stable at 600 °C, and/or the phenol or lactone groups that are only partially removed at 600 °C [44]. X-ray photoelectron spectroscopy (XPS) analysis shows that nitrogen is not present in the surface of the CNT-O and CNT-BM catalysts, whereas a significant amount of nitrogen (3.7 wt%) was incorporated in the CNT-BM-M catalyst surface as a result of the treatment with the N-precursor. Three different N-groups were detected, quaternary nitrogen, pyrrole and pyridinic structures [36]. The most abundant was the pyridinic structure, corresponding to 57 % of the total nitrogen, followed by pyrrole, with 32%, and lastly the quaternary nitrogen, with 11%.

The stability of these groups was analyzed by thermogravimetric analysis (TGA), under helium atmosphere until 900 °C. A weight loss lower than 1% was observed until 500 °C, and only 7% between 500 and 900 °C. The weight loss at higher temperatures was mainly attributed to the decomposition of the O-containing functional groups, since the CNT-BM catalyst presented a similar weight loss [36].

#### 3.2. Catalytic activity of the catalysts

##### 3.2.1. Batch operating mode

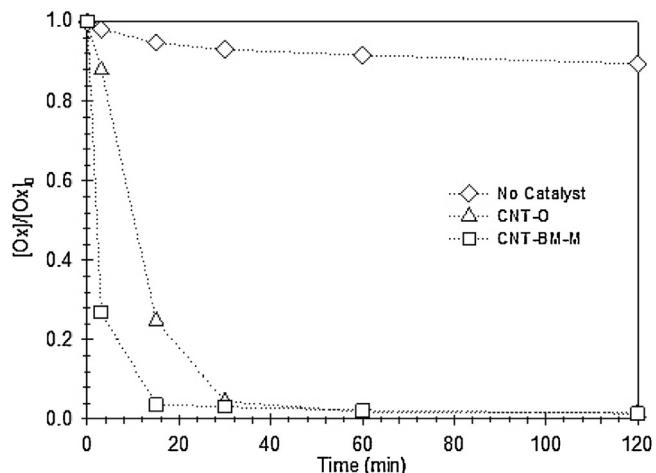


**Fig. 1.** Normalized phenol concentration ( $Ph/Ph_0$ ) versus time for the screening of different catalysts in batch CWO experiments ( $160\text{ }^\circ\text{C}$  and 6 bar  $P/\text{O}_2$ ).

**3.2.1.1. Screening experiments.** The catalytic activity of the CNT materials was initially evaluated in screening experiments using phenol as model pollutant in batch operating conditions. As Fig. 1 shows, practically no phenol conversion was observed in the absence of a catalyst. In contrast, the phenol conversions observed after 2 h of reaction were 40, 68 and 98% for CNT-O, CNT-BM and CNT-BM-M catalysts, respectively. It is clear that the treatments applied to the original CNTs, both ball milling and the N-doping approach, were beneficial to the catalytic activity of these materials, due to the increase in  $S_{\text{BET}}$ , providing additional catalytic surface accessible for the reaction, and due to the incorporation of N-functionalities (basic active sites), as shown in Table 1, which have already been identified by some authors [27,28] as beneficial to CWO. Adsorption experiments were also performed using the same operating conditions, but with nitrogen instead of air in the gas phase. For CNT-O and CNT-BM materials, the contribution of adsorption was very low, with around 5% of phenol removal being achieved after 2 h. For CNT-BM-M, this contribution was higher, near 15% for the same period. The TOC removal at the end of the experiments was also evaluated. Only the CNT-BM and CNT-BM-M materials presented considerable TOC removals, both around 50%. Since the phenol removal was considerably higher for the CNT-BM-M catalyst (98%) than for CNT-BM (68%), but the TOC removal was similar in both cases, the incorporation of N-functionalities on the CNTs seems to induce a different affinity between the catalyst, dissolved oxygen and the parent pollutant present in the aqueous solution.

According to the literature, severe operating conditions are needed to remove phenol by non-catalytic WO. For instance, phenol and TOC removals of 21 and 12%, respectively, were obtained at  $215\text{ }^\circ\text{C}$  and 2 bar  $P/\text{O}_2$ . When the temperature and oxygen partial pressure were raised to  $265\text{ }^\circ\text{C}$  and 9 bar, respectively, the phenol and TOC removal increased to 90 and 73 %, respectively [45]. Carbon materials have already been tested as potential catalysts for phenol degradation. MWCNTs treated with  $\text{H}_2\text{SO}_4$  achieved phenol and TOC removals of 100 and 57 %, respectively, after 2 h of reaction at  $160\text{ }^\circ\text{C}$  and 40 bar of total pressure [28]. However, this catalyst showed little stability, with the phenol conversions decreasing to 10% in a second run.

The original catalyst (CNT-O) and that achieving the highest catalytic activity for phenol removal (CNT-BM-M) were also evaluated in the oxidation of oxalic acid, as this is a common intermediary (or end-product) found when advanced oxidation processes are applied. These experiments were performed under less severe operating conditions, as it is known from our previous reports [28]

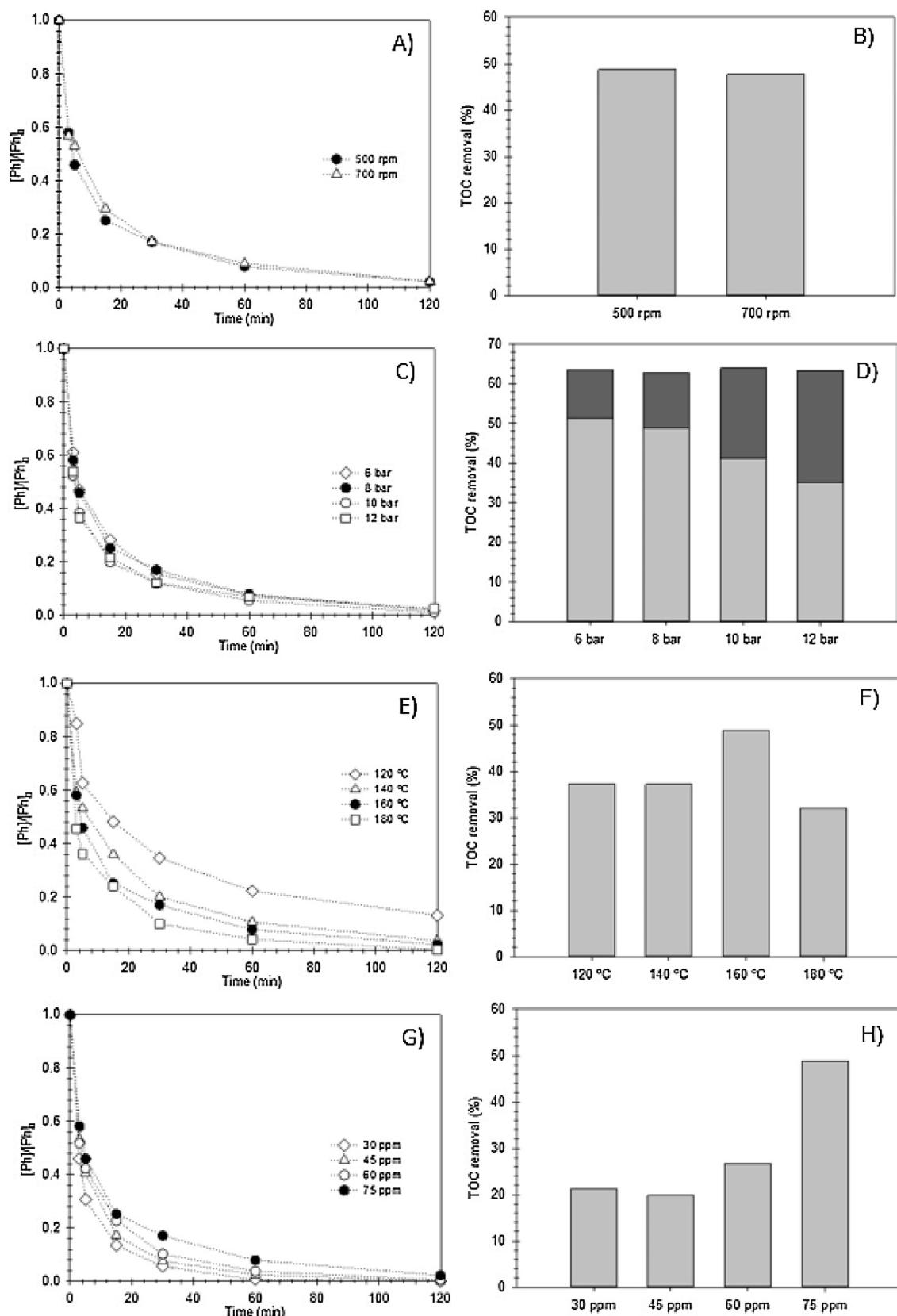


**Fig. 2.** Normalized oxalic acid concentration ( $Ox/Ox_0$ ) versus time for the screening of different catalysts in batch CWO experiments ( $140\text{ }^\circ\text{C}$  and 5 bar  $P/\text{O}_2$ ).

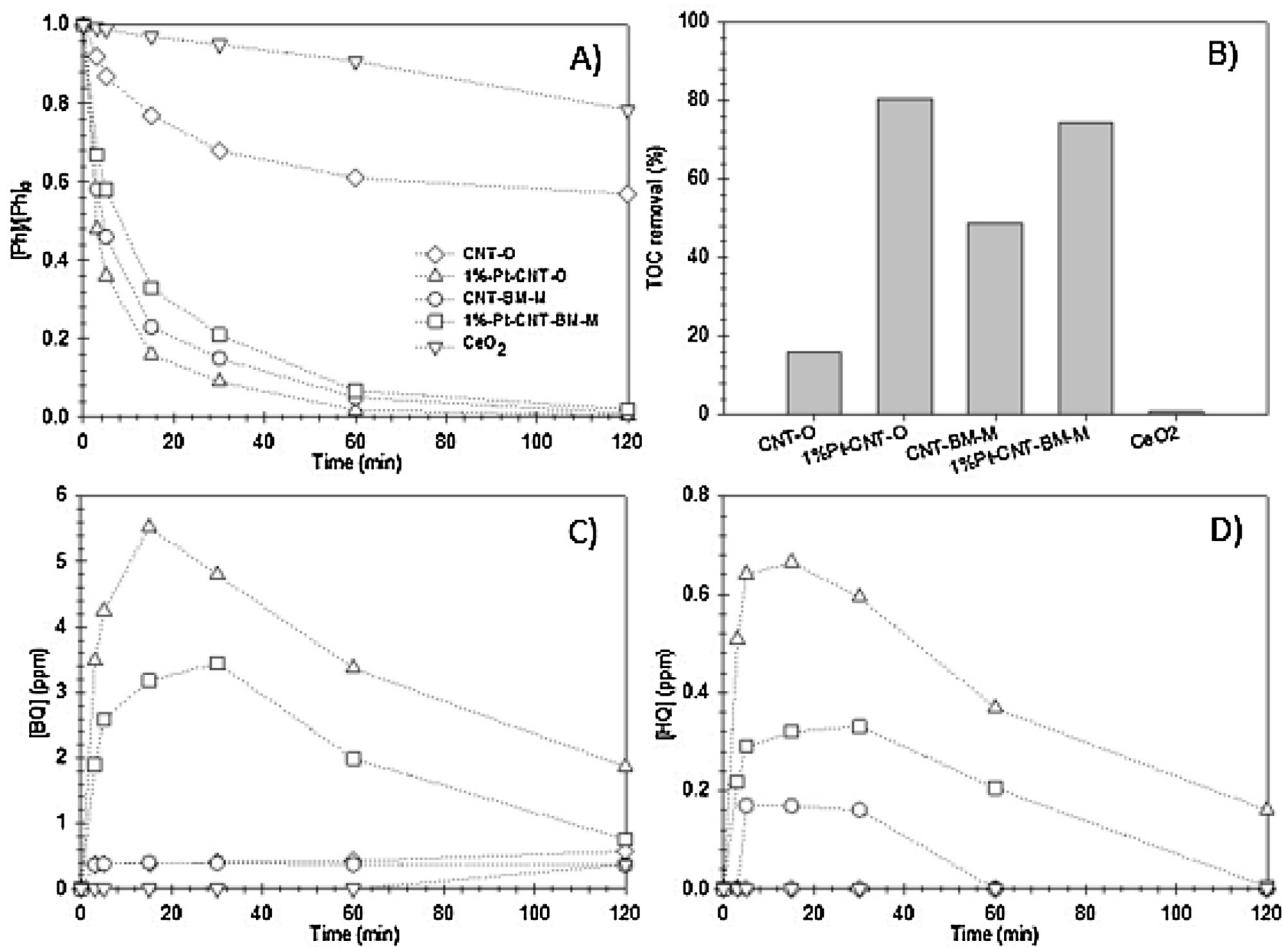
that this compound is easier to remove than phenol. Fig. 2 shows that, in the absence of a catalyst, the oxalic acid removal is low (10%). Both CNT-O and CNT-BM-M can completely remove oxalic acid after 30 and 15 min of reaction, respectively. Again, the N-doped catalyst presented a higher catalytic activity than the original one. Adsorption experiments were also performed under the same operating conditions. Oxalic acid adsorption was not observed with CNT-O, while CNT-BM-M adsorbed 32% of oxalic acid in the first 3 min, showing that N-groups increase the adsorption of this compound. Results of the CWO of oxalic acid in the literature show that this compound is easily removed at mild operating conditions, in the presence of an active catalyst. For instance, Rocha et al. [27] studied the degradation of oxalic acid (initial concentration of  $1000\text{ mg L}^{-1}$ ) over nitric acid, urea and thermally treated MWCNTs, total degradation being obtained after 15 min of reaction at  $140\text{ }^\circ\text{C}$  and 40 bar of total pressure in the case of the sample prepared with urea, while 30 min were needed in the case of MWCNTs subjected to only nitric acid and thermal treatment [28].

**3.2.1.2. Effect of operating conditions.** Bearing in mind the best performance obtained with CNT-BM-M in CWO, different operating conditions were studied with this catalyst using phenol as model pollutant. The standard operating conditions selected for these experiments were: (i) a stirring speed of 500 rpm; (ii)  $160\text{ }^\circ\text{C}$ ; (iii) 8 bar of oxygen partial pressure; (iv)  $75\text{ mg L}^{-1}$  of phenol; and (v) 0.2 g of catalyst. An experiment without catalyst was also performed and no phenol or, as expected, TOC removal was observed, in agreement with the non-catalytic results obtained in Fig. 1. Fig. 3(A, C, E, G) and (B, D, F, H) shows the normalized phenol concentration (left) and TOC removal (right), respectively, for each set of operating conditions changing one parameter only while keeping the others constant (the full symbols correspond to the standard operating conditions). Fig. 3A and B shows that the stirring speed in the range studied (500–700 rpm) has no effect on the degradation of phenol, which suggests the absence of external mass transfer limitations.

The dissolved oxygen concentration, controlled by the oxygen partial pressure, had little effect on the phenol removal (Fig. 3C), increasing only slightly when the oxygen partial pressure increases. On the contrary, a higher amount of dissolved oxygen originated a lower TOC removal (Fig. 3D), from 51 to 35% at 6 and 12 bar of oxygen partial pressure, respectively. Differences in the gas-phase equilibrium concentration of the organic products formed can be the cause of this unexpected result, and not necessarily differences in the degradation of the parent pollutant (as shown in Fig. 3C),



**Fig. 3.** Normalized phenol concentration ( $\text{Ph}/\text{Ph}_0$ ) versus time, and TOC removal after 120 min, for the experiments performed with the CNT-BM-M catalyst in the batch reactor. (A and B)—stirring speed variation; (C and D)—Oxygen partial pressure variation; (E and F)—Temperature variation; (G and H)—Initial phenol concentration variation. Standard conditions: 500 rpm; 160 °C; 8 bar and 75 mg L<sup>-1</sup> of phenol (full circles).



**Fig. 4.** (A) Normalized phenol concentration ( $\text{Ph}/\text{Ph}_0$ ), (B) TOC removal after 120 min, (C) benzoquinone (BQ) formation and (D) hydroquinone (HQ) formation in batch CWO experiments ( $160^\circ\text{C}$ ; 8 bar  $\text{P}/\text{O}_2$ ).

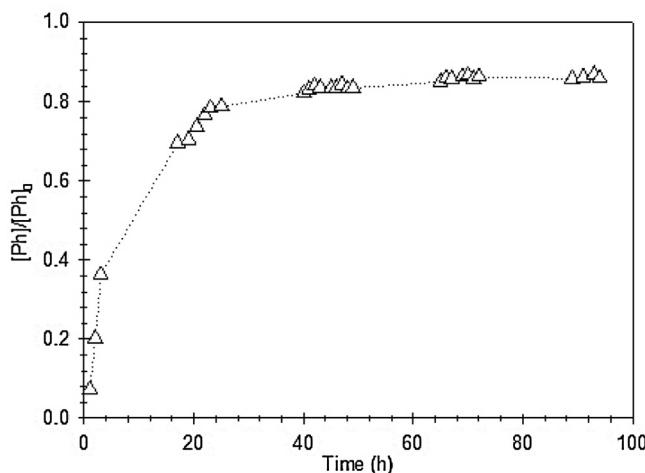
i.e. a high pressure could originate a higher concentration of by products in the liquid phase, and thus, a higher TOC content and an apparent lower TOC removal. In an attempt to confirm this hypothesis, the samples obtained after the depressurization and cooling of the reactor were also analyzed. The TOC removal, after fast depressurization and cooling of the reactor, was the same for all experiments, as shown in Fig. 3D (black bars), which is in agreement with the formulated hypotheses, showing that the dissolved oxygen concentration has little effect on the reaction. This behavior has already been observed in the degradation of phenol [46,47]. It should be highlighted that, in this range of pressures, the dissolved oxygen concentration is always above the stoichiometric concentration needed for total mineralization of phenol.

As Fig. 3E and F shows, temperature has a significant effect on the reaction. After 1 h of reaction, the phenol removals observed were 78, 89, 92 and 96% at 120, 140, 160 and 180 °C, respectively. An almost complete removal of phenol (>95%) was achieved after 2 h of reaction at all temperatures tested, except at 120 °C, (87% phenol removal). However, regarding the TOC content, the maximum removal (49%) was observed at 160 °C, decreasing to 32% at 180 °C. The lower TOC removal observed at 180 °C suggests that polymerization of phenol might occur, leading to catalyst deactivation, as already reported [47].

The influence of the initial phenol concentration is shown in Fig. 3G and H, where it is observed that the phenol removal is slightly higher for lower initial concentrations. In terms of mass of phenol removed, a higher initial concentration leads to a higher amount of phenol removed. After 15 min of reaction, the phenol

removals observed were 87, 83, 77 and 75 %, corresponding to 22, 32, 38 and 47  $\text{mg L}^{-1}$  of phenol removed, for initial concentrations of 30, 45, 60 and 75  $\text{mg L}^{-1}$ , respectively, i.e. the mass of pollutant removed increases with the phenol concentration. The highest removal of carbon content was also obtained for the initial phenol concentration of 75  $\text{mg L}^{-1}$ . The values observed were 5, 6, 10 and 22  $\text{mg TOC L}^{-1}$  removed for initial phenol concentrations of 30, 45, 60 and 75  $\text{mg L}^{-1}$ , respectively.

**3.2.1.3.  $\text{CNT-BM-M}$  vs.  $\text{Pt-supported}$  and  $\text{CeO}_2$  catalysts.** Experiments comparing the performance of carbon nanotubes with more conventional catalysts were also performed. The conventional catalysts used for comparison were: 1% Pt (wt%) supported on CNT-O or CNT-BM-M, as well as cerium oxide ( $\text{CeO}_2 - S_{\text{BET}} = 98 \text{ m}^2 \text{ g}^{-1}$ ). Fig. 4A shows that  $\text{CeO}_2$  and CNT-O present much lower activity than the other catalysts. The 1%-Pt-CNT-O catalyst has the highest activity among all the catalysts tested; nevertheless, the phenol removals observed with the CNT-BM-M sample were only slightly lower. For example, the phenol removals at 30 min of reaction were 91 and 85% for 1%-Pt-CNT-O and CNT-BM-M, respectively. The TOC removals at the end of the experiment, shown in Fig. 4B, were much higher for the Pt-supported catalysts: 80 and 75%, for 1%-Pt-CNT-O and 1%-Pt-CNT-BM-M, respectively, compared to 49% for CNT-BM-M. In these experiments, the concentrations of 1,4-benzoquinone and hydroquinone were also determined (Fig. 4C and D). These compounds are common intermediates in the CWO of phenol, and are known as much more toxic than the parent pollutant [48]. Even though the values are low, it is possible to see that the



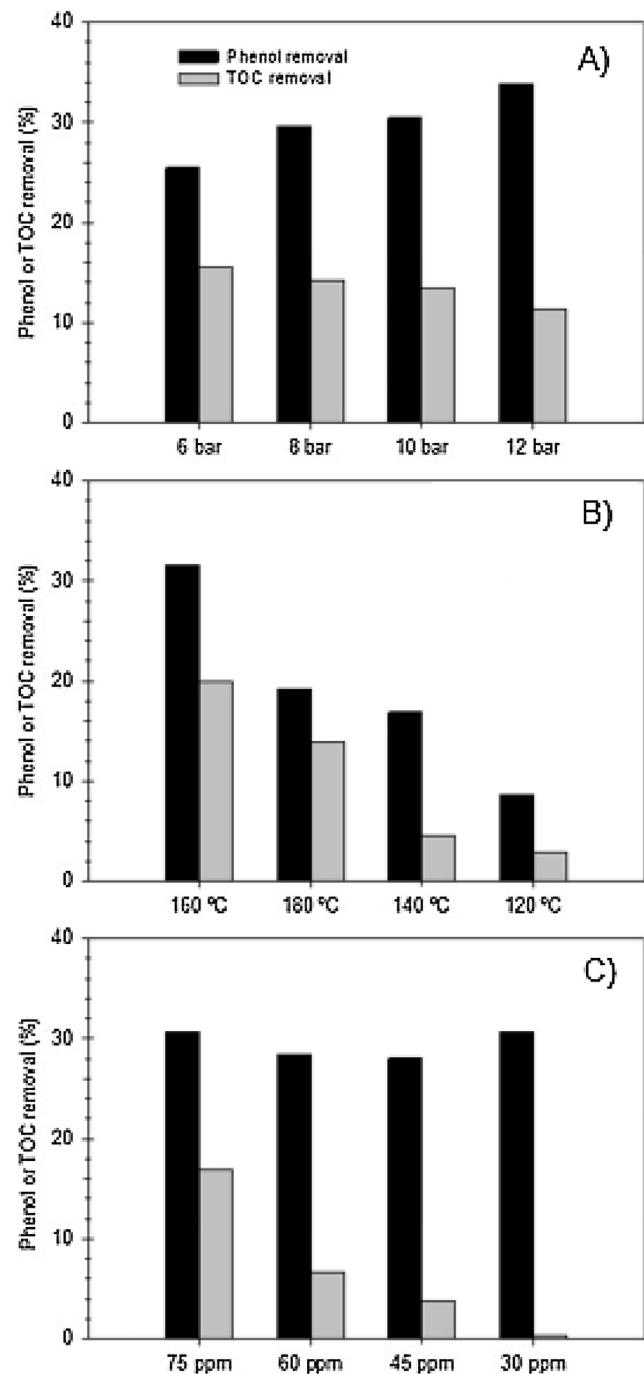
**Fig. 5.** Normalized phenol concentration ( $\text{Ph}/\text{Ph}_0$ ) versus time, in continuous mode CWO. ( $160^\circ\text{C}$ ; 5.2 bar  $\text{P}/\text{O}_2$ ; liquid flow rate of  $0.25 \text{ mL min}^{-1}$ ).

concentration of these compounds is much higher when platinum is used as catalyst, and the toxicity of the treated effluent is expected to be higher as well, in particular for a low hydraulic retention time. It is important to note that the formation of carbonaceous deposits on the surface of the catalyst and the over-oxidation of Pt were not evaluated. However, these phenomena are known to originate the deactivation of Pt-based catalysts in CWO [15,16,49]. Taking into account the high Pt demands and costs, Pt-free CNT-BM-M is a better alternative for waste water treatment by CWO, achieving high phenol removal in addition to the fact that it can be prepared by a cost effective and easy to handle method, avoiding the use of solvents and production of wastes.

### 3.2.2. Continuous operating mode

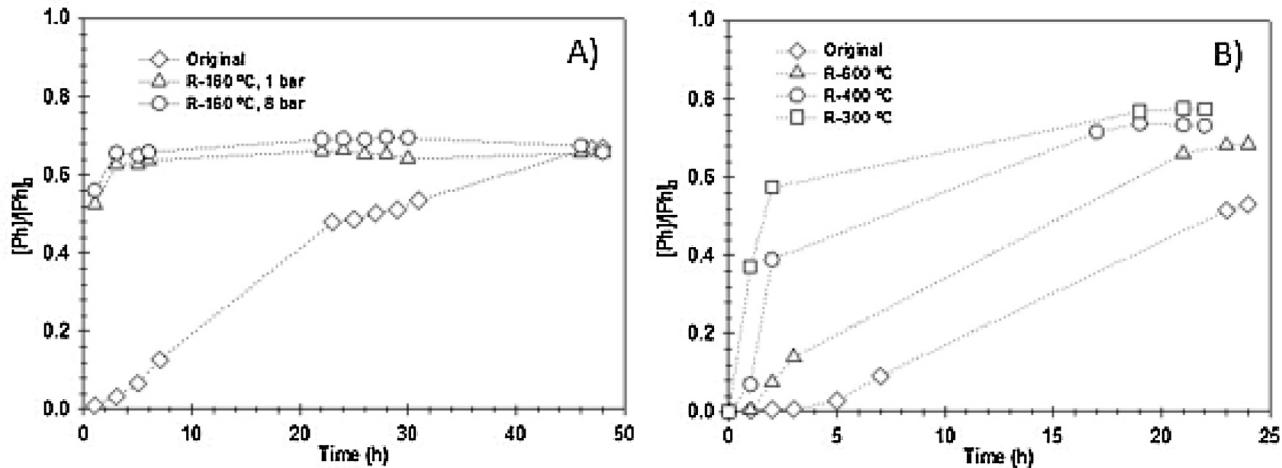
**3.2.2.1. CNT-BM-M stability and steady state.** Fig. 5 shows the results obtained in an experiment with the CNT-BM-M catalyst in continuous mode, in order to check the catalyst stability and the time needed to reach a steady state. The catalyst is severely deactivated in the first 30 h of reaction; the deactivation is much less pronounced after 40 h, with a phenol removal near 15% after 94 h. The deactivation is expected to be due to the deposition of phenolic polymers on the surface of the catalyst [47], which will reduce the area of contact between the catalyst and the contaminants. To confirm this, TG analysis was performed on the catalyst after the reaction (not shown). The mass loss was similar to the fresh catalyst until  $450^\circ\text{C}$ . At higher temperatures, the used catalyst presents a mass loss higher than the fresh catalyst. At the end of the analysis ( $T = 900^\circ\text{C}$ ), the mass loss of the used catalyst was near 13%, whereas the fresh catalyst presented only 8%, which suggests that phenolic polymers are deposited on the catalyst surface. This behavior has already been observed in the CWO of phenol over activated carbons [21,22]. Other forms of deactivation, such as modification of the N-functional groups might also occur.

**3.2.2.2. CNT-BM-M: effect of operating conditions.** The effect of different operating conditions was also evaluated in the continuous reactor. These experiments were performed with the CNT-BM-M catalyst and phenol as model pollutant. The standard conditions were the same as in the batch experiments ( $T = 160^\circ\text{C}$ ,  $\text{P}/\text{O}_2 = 8 \text{ bar}$  and  $75 \text{ mg L}^{-1}$  phenol). The catalytic tests were performed in three different sets of experiments, in each set varying one parameter ( $\text{P}/\text{O}_2$ ,  $T$  or initial phenol concentration) while keeping the others constant. For each set of experiments, the reaction was carried out until near steady state (48 h). Then, the value of the parameter under study was changed and the experiment was



**Fig. 6.** Phenol and TOC removal for the experiments with the CNT-BM-M catalyst in continuous mode CWO. (A)—Oxygen partial pressure variation; (B)—Temperature variation; (C)—Initial phenol concentration variation. Standard conditions:  $160^\circ\text{C}$ ; 8 bar and  $75 \text{ mg L}^{-1}$  of phenol. Please note that the variation of oxygen partial pressure, temperature and initial phenol concentration is shown in the same order the respective parameter was changed during the set of experiments.

carried out for more 24 h to achieve a new steady state. In the case where the temperature was the parameter in study, the oxygen partial pressure was also adjusted to maintain the dissolved oxygen concentration constant. An experiment without catalyst was performed to assess the non-catalytic contribution of the oxidation process. In this experiment, no phenol or TOC removal was observed. An adsorption experiment, using nitrogen instead of the oxidizing agent (oxygen), was also performed. After 3 h of reaction, there was no phenol nor TOC removal.



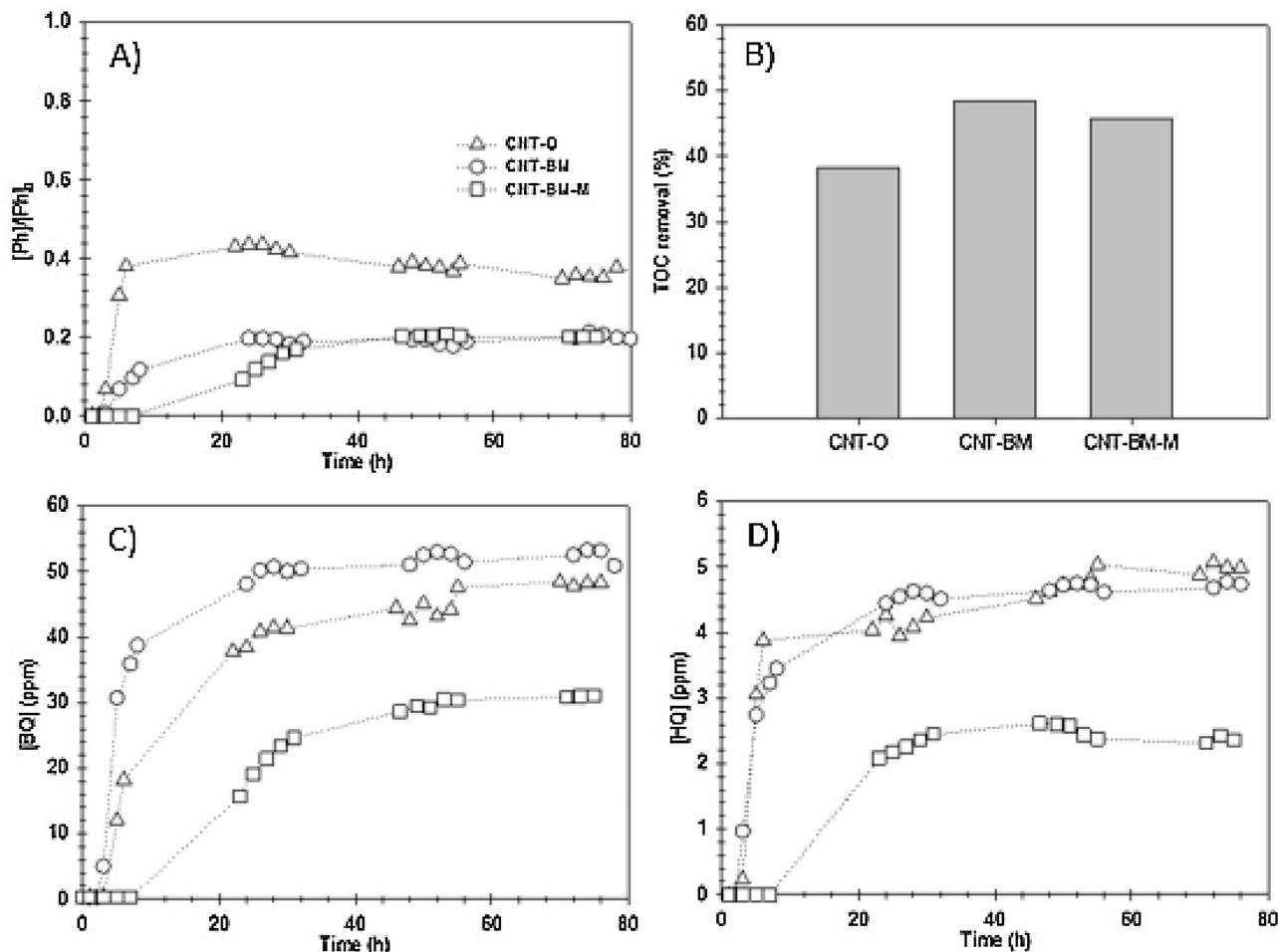
**Fig. 7.** Normalized phenol concentration ( $Ph/Ph_0$ ) versus time, in continuous mode CWO with CNT-BM-M catalyst after different regeneration attempts: (A) near operating conditions, (B) at high temperatures.

**Fig. 6A** shows the influence of the dissolved oxygen concentration, represented by the oxygen partial pressure, on the phenol and TOC removals. The phenol removal increased from 26 to 34% with the increase of the dissolved oxygen concentration that is achieved when increasing  $P/O_2$  from 6 to 12 bar, respectively. The TOC removals observed for the different dissolved oxygen concentrations were quite similar (differences lower than 5%), but slightly lower for higher dissolved oxygen concentrations. Both phenol and TOC removals observed for the different dissolved oxygen concentrations are close to each other, confirming the low influence of this parameter. These results are in agreement with those obtained in batch operation (Figs. 3C and 3D). Once again, temperature presented a more pronounced effect on the reaction for the range of temperatures and pressures selected in the present work (Fig. 6B), as also observed in batch conditions (Fig. 3E). A maximum of phenol and TOC removal occurred at 160 °C, decreasing when the temperature was changed to 180 or 140 °C, as it happened with the TOC removal in the batch experiments (Fig. 3F), confirming that temperatures higher than 160 °C can be detrimental to the efficiency of the process. The decrease of phenol and TOC removals at 180 °C is probably more evident in continuous mode due to the constant feeding of this pollutant and the constant formation of by-products/C-deposits that strongly deactivate the catalyst when this temperature is used. The initial phenol concentration had little effect on the percentage of removed phenol, with differences lower than 3% between all the initial concentrations tested. However, the amount of phenol removed increased for higher initial concentration, from 10 to 23 mg L<sup>-1</sup> between 30 and 75 mg L<sup>-1</sup>, respectively, as also observed in the batch experiments. The variation of the percentage of TOC removal with the initial concentration was much more noticeable, increasing from almost 0–17% between 30 and 75 mg L<sup>-1</sup>, which corresponds to a carbon content removal between almost 0 and 8 mg L<sup>-1</sup>, respectively. Thus, a higher initial concentration allows a superior removal of both mass of phenol and carbon content, which shows that, in this range of concentrations, the process is more efficient when higher initial concentrations are used (also shown in Fig. 3H).

**3.2.2.3. Regeneration attempts of the CNT-BM-M catalyst.** Since the CNT-BM-M catalyst is strongly deactivated in the first 24 h of reaction (as shown in Fig. 5), regeneration attempts were performed to assess if it was possible to return the catalyst to its original activity. A washing step (not shown) was performed after testing at standard reaction conditions (160 °C, 8 bar and 75 mg L<sup>-1</sup> of

phenol). The washing consisted in passing water through the catalyst bed for 2 h at room temperature under nitrogen flow. No regeneration of the catalyst was observed. Regeneration near the operating conditions was tested next. Two regeneration attempts were performed at different pressures, one at 1 bar and another at 8 bar, both at 160 °C under oxygen atmosphere. As Fig. 7A shows, neither attempt was efficient at regenerating the catalyst, since the value of the phenol removal at the beginning of the new experiments (after regeneration at 1 or 8 bar) was the same as the end value of the original experiment. Regeneration by thermal treatment at higher temperatures was then attempted. Temperatures of 600, 400 and 300 °C were used under nitrogen atmosphere at 1 bar. The regeneration attempts were performed one after another, from the highest to the lowest temperature, using the same catalyst. As Fig. 7B shows, an almost complete phenol removal was observed in the first 5 h of reaction with the fresh catalyst (original), dropping to 47% after 24 h. When a temperature of 600 °C was used, a significant regeneration of the catalyst was observed, the phenol removal being higher than 90% in the first 2 h of reaction after regeneration. However, deactivation of the catalyst started sooner, lowering the phenol removal to 32% after 24 h of reaction. This shows that, even though a significant regeneration was achieved, the catalyst was not completely regenerated. The other temperatures tested led to much lower regeneration of the catalyst, with 61 and 43% of phenol removed after 2 h of reaction, upon regeneration at 400 and 300 °C, respectively. Thus, a temperature of 600 °C seems to be effective at regenerating the catalyst for the first hours of reaction, and regeneration cycles could be applied every 5 h in a real implementation of the process.

**3.2.2.4. Intensification conditions.** An experiment was carried out under intensified conditions to study the performance of the process for higher concentrations. An initial phenol concentration of 500 mg L<sup>-1</sup> was used. To maintain constant the mass of catalyst/mass flow of phenol (W/F) ratio, the catalyst mass was increased to 1.3 g, and CNT-O, CNT-BM and CNT-BM-M samples were compared. The oxygen partial pressure was also raised to 12 bar, while the temperature remained at 160 °C. A blank experiment was also performed at such conditions, namely without any catalyst, and no phenol removal was observed. CNT-O presented a variation in the phenol removal during the experiment, from 55 to 64%, from 24 to 72 h, respectively (Fig. 8A). These values were much lower than those obtained by using the other two catalysts. Both CNT-BM and CNT-BM-M achieved a phenol removal of 80%



**Fig. 8.** (A) Normalized phenol concentration ( $\text{Ph}/\text{Ph}_0$ ), (B) TOC removal after 76 h, (C) benzoquinone formation and (D) hydroquinone formation in continuous mode CWO experiments with the CNT-O, CNT-BM and CNT-BM-M ( $160^\circ\text{C}$  and 12 bar  $\text{P}/\text{O}_2$ ).

after 48 h, which remained stable until the end of the experiment; however, as Fig. 8A shows, in the first 30 h of reaction the phenol removal was higher with CNT-BM-M, especially in the first 7 h where phenol was completely removed. An adsorption experiment was carried out to check if the complete removal of phenol in the first hours of reaction was due to adsorption. At the second hour of the adsorption experiment, a reduction of 21% in the phenol concentration was observed. From the third hour onwards, no adsorption was detected, which means that the catalyst was oxidizing phenol rather than eliminating the pollutant from the liquid by adsorption. These results show that the incorporation of N-groups is beneficial to the reaction, increasing significantly the phenol removal. However, this catalyst is deactivated, probably due to the formation of phenolic polymers that deposit on the surface of the catalyst, blocking the access to the functional groups. Once all the functional groups become inaccessible, the phenol removal is equal to the catalyst without functional groups (CNT-BM). It is important to refer that phenol is a complicated pollutant in comparison to many others due to the formation of polymeric deposits. For this reason, it was selected for the present work, much better process performances being expected for the degradation of other types of pollutants.

Fig. 8B shows the TOC removal in the steady state. Values close to 50% were achieved with both CNT-BM and CNT-BM-M catalysts. The concentrations of 1,4-benzoquinone and hydroquinone are shown in Fig. 8C and D, respectively. Much lower concentrations of these intermediaries were produced with the CNT-BM-M

catalyst. With this catalyst, in the first 7 h, none of these compounds was detected, while after 72 h, their concentrations increased to 31 and 2.4 mg L<sup>-1</sup>, respectively. For the CNT-BM catalyst, the concentrations of these compounds were 53 and 4.7 mg L<sup>-1</sup>, respectively. In these experiments, a significant concentration of maleic acid was also identified. This was the only intermediary detected in the first 7 h of reaction with the CNT-BM-M catalyst, reaching 17 mg L<sup>-1</sup>. When the steady state was achieved, the values observed for this compound were 20, 20 and 25 mg L<sup>-1</sup> for the CNT-O, CNT-BM and CNT-BM-M catalysts, respectively. Contrary to the other intermediates identified, the maleic acid concentration was slightly higher for CNT-BM-M.

Regarding the mechanism for phenol oxidation in the CWO process over carbon nanotubes, three main pathways can occur simultaneously: (i) formation of by products (mostly the aromatic quinones, 1,4-benzoquinone and hydroquinone); (ii) formation of carbonaceous deposits which block the access to the active sites; (iii) direct phenol mineralization into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The aromatic quinones are then oxidized into low molecular weight carboxylic acids (mainly maleic acid). These species, and probably a fraction of the carbonaceous deposits, are further oxidized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The role of N-functionalities is to increase the electron density on the surface of the carbon material, which promotes the oxidation reactions taking place during the degradation and mineralization of phenol [17,37,50].

In order to better understand the deactivation of the CNT-BM-M catalyst, XPS and TG analyses were performed to the material,

**Table 2**

Mass percentage of the different elements at the surface of the materials.

Sample/Element (m%)	%C	%O	%N
CNT-BM-M fresh	95.68	0.67	3.65
CNT-BM-M after reaction	94.60	3.27	2.13
CNT-BM-M after regeneration	96.67	1.23	2.10

**Table 3**

N-functionalities at the surface of the materials.

Sample/N-functionalities (%)	N-5	N-6	N-Q
CNT-BM-M fresh	32.1	57.4	10.5
CNT-BM-M after reaction	43.7	45.3	11.0
CNT-BM-M after regeneration	34.7	53.6	11.7

before reaction, after reaction and after regeneration at 600 °C under nitrogen flow. **Tables 2 and 3** show the results obtained by XPS.

**Table 2** shows the proportions of the different elements present on the surface of the catalyst. It is possible to see that the N percentage decreases after the reaction, and the regeneration does not seem to increase it to the original value. However, the type of N-functionalities (**Table 3**) differs after the reaction, increasing the pyrrole (N-5) and decreasing the pyridine (N-6). With the regeneration, the proportions of the N-groups return to near the original values, increasing the amounts of N-6 groups. Since the N-6 groups have already been proposed as the most appropriate for oxidation reactions [37], the increase in the amount of these groups can be one of the causes for the partial recovery of the catalytic activity of the materials after regeneration (Section 3.2.2.3. Regeneration attempts of the CNT-BM-M catalyst).

A TG analysis under nitrogen atmosphere was also performed to the samples (**Fig. 9**). It is possible to see that the material after the reaction has a more significant mass loss, starting around 200 °C, while with the fresh catalyst, the mass loss started near 450 °C. After the regeneration, the mass loss is almost identical to the fresh catalyst. The removal of carbonaceous deposits of the surface of the material with the regeneration step (seen by the decrease of the mass loss after regeneration) is also responsible for recovering the catalytic activity of the catalyst.

#### 4. Conclusions

Carbon nanotubes with N-groups (CNT-BM-M), namely, quaternary nitrogen (N-Q), pyrrolic (N-5) and pyridinic (N-6) groups, showed high catalytic activity for phenol removal in batch and continuous operation. Complete phenol removal and 50% TOC removal was obtained in the batch reactor after 2 h of reaction at 160 °C and 6 bar of oxygen partial pressure. In the continuous mode reactor, phenol and TOC removals of 80 and 50%, respectively, were achieved in steady state, at 160 °C and 12 bar of oxygen partial pressure, with an initial phenol concentration of 500 mg L<sup>-1</sup>.

The dissolved oxygen concentration, controlled by the oxygen partial pressure, had only a small effect on the phenol and TOC removals, considering the range under study. The temperature had a significant influence on the reaction. The temperature increase had a beneficial effect until 160 °C. At higher temperatures, a decrease in the phenol and TOC removals was detected, probably due to the formation of carbonaceous deposits, leading to the deactivation of the catalyst. The process was more efficient for higher initial phenol concentrations, in the range of concentrations studied (30–75 mg L<sup>-1</sup>), an advantage to treat highly polluted wastewaters.

Thermal treatments near the operating conditions had no regenerative effects on the CNT-BM-M catalyst. Thermal treatment at 600 °C achieved good regeneration of the catalyst; however, the deactivation of the regenerated catalyst started much sooner than that of the fresh catalyst, which means that the regeneration was not complete, and that short regeneration cycles (ex. 5 h) should be applied to maintain a high or even complete degradation of phenol.

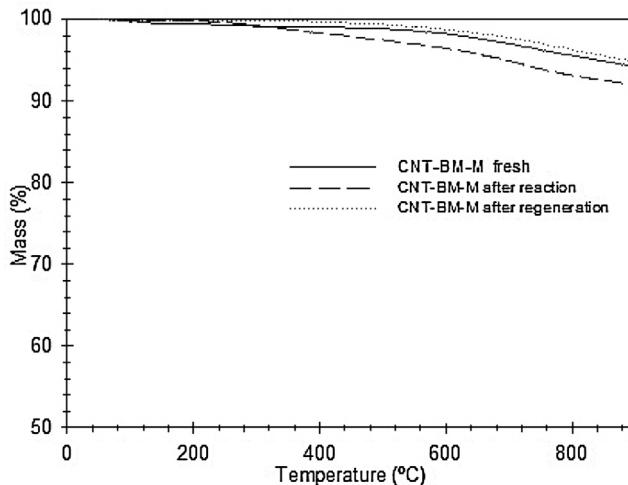
#### Acknowledgments

This work was supported by projects: FREECATS, European Union 7th FP, grant #280658; POCI-01-0145-FEDER-006984 - Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) - and by national funds through FCT - Fundação para a Ciência e a Tecnologia. D. Santos and O.S.G.P. Soares acknowledge grants received from FCT (PD/BD/105983/2014 and SFRH/BPD/97689/2013, respectively). A.M.T. Silva acknowledges the FCT Investigator 2013 Programme (IF/01501/2013), with financing from the European Social Fund and the Human Potential Operational Programme. The authors also acknowledge Dr. Carlos M. Sá (CEMUP) for assistance with XPS analyses.

#### References

- [1] F. Stuber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias, A. Fabregat, *Top. Catal.* 33 (2005) 3–50.
- [2] J. Levec, A. Pintar, *Catal. Today* 124 (2007) 172–184.
- [3] J. Wang, W. Fu, X. He, S. Yang, W. Zhu, *J. Environ. Sci.* 26 (2014) 1741–1749.
- [4] A. Rodriguez, G. Ovejero, M.D. Romero, C. Diaz, M. Barreiro, J. Garcia, *J. Supercrit. Fluids* 46 (2008) 163–172.
- [5] K.-H. Kim, S.-K. Ihm, *J. Hazard. Mater.* 186 (2011) 16–34.
- [6] C. Lousteau, M. Besson, C. Descorme, *Catal. Today* 241 (2015) 80–85 (Part A).
- [7] G. de los Monteros, A. Lafaye, G. Cervantes, J. DelAngel, G. Barbier Jr., *Catal. Today* 258 (2015) 564–569 (Part 2).
- [8] S. Keav, A. Martin, J. Barbier Jr., D. Duprez, *Catal. Today* 151 (2010) 143–147.
- [9] C. Diaz, G. Ovejero, J.L. Sotelo, A. Rodriguez, J. Garcia, *Catalytic wet air oxidation of aqueous solution of phenol over Pt/CNF catalyst*, in: *Proceedings of European Congress of Chemical Engineering (ECCE-6)*, Copenhagen, 2007.
- [10] A. Pintar, J. Batista, T. Tisler, *Appl. Catal. B Environ.* 84 (2008) 30–41.
- [11] F. Arena, C. Italiano, L. Spadaro, *Appl. Catal. B Environ.* 115–116 (2012) 336–345.
- [12] A. Fortuny, C. Bengoa, J. Font, A. Fabregat, *J. Hazard. Mater.* 64 (1999) 181–193.
- [13] F. Schmit, L. Bois, F. Chassagneux, C. Descorme, *Catal. Today* 258 (2015) 570–575 (Part 2).
- [14] S. Yang, W. Zhu, J. Wang, Z. Chen, J. Hazard. Mater. 153 (2008) 1248–1253.
- [15] D.-K. Lee, D.-S. Kim, T.-H. Kim, Y.-K. Lee, S.-E. Jeong, N.T. Le, M.-J. Cho, S.D. Hanam, *Catal. Today* 154 (2010) 244–249.

**Fig. 9.** TG analysis of the CNT-BM-M samples, before reaction, after reaction and after regeneration.



[16] R. Kouraichi, J.J. Delgado, J.D. López-Castro, M. Stitou, J.M. Rodríguez-Izquierdo, M.A. Cauqui, *Catal. Today* 154 (2010) 195–201.

[17] H. Chen, G. Yang, Y. Feng, C. Shi, S. Xu, W. Cao, X. Zhang, *Chem. Eng. J.* 198 (2012) 45–51.

[18] H.T. Gomes, B.F. Machado, A. Ribeiro, I. Moreira, M. Rosario, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, J. Hazard. Mater. 159 (2008) 420–426.

[19] M.E. Suarez-Ojeda, F. Stüber, A. Fortuny, A. Fabregat, J. Carrera, J. Font, *Appl. Catal. B Environ.* 58 (2005) 105–114.

[20] M. Santiago, F. Stüber, A. Fortuny, A. Fabregat, J. Font, *Carbon* 43 (2005) 2134–2145.

[21] B. Larruy, A. Ayude, J. Font, A. Fortuny, C. Bengoa, A. Fabregat, F. Stüber, *Chem. Eng. Sci.* 62 (2007) 5564–5566.

[22] M.E. Suarez-Ojeda, A. Fabregat, F. Stüber, A. Fortuny, J. Carrera, J. Font, *Chem. Eng. J.* 132 (2007) 105–115.

[23] F. Stüber, K.M. Smith, M. Baricot Mendoza, R.R.N. Marques, A. Fabregat, C. Bengoa, J. Font, A. Fortuny, S. Pullket, G.D. Fowler, N.J.D. Graham, *Appl. Catal. B Environ.* 110 (2011) 81–89.

[24] S. Morales-Torres, A.M.T. Silva, A.F. Pérez-Cadenas, J.L. Faria, F.J. Maldonado-Hódar, J.L. Figueiredo, F. Carrasco-Marín, *Appl. Catal. B Environ.* 100 (2010) 310–317.

[25] R.P. Rocha, J. Restivo, J.P.S. Sousa, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo, *Catal. Today* 241 (2015) 73–79 (Part A).

[26] A.C. Apolinario, A.M.T. Silva, B.F. Machado, H.T. Gomes, P.P. Araujo, J.L. Figueiredo, J.L. Faria, *Appl. Catal. B Environ.* 84 (2008) 75–86.

[27] R.P. Rocha, J.P.S. Sousa, A.M.T. Silva, M.F.R. Pereira, J.L. Figueiredo, *Appl. Catal. B Environ.* 104 (2011) 330–336.

[28] R.P. Rocha, A.M.T. Silva, S.M.M. Romero, M.F.R. Pereira, J.L. Figueiredo, *Appl. Catal. B Environ.* 147 (2014) 314–321.

[29] S. Yang, X. Li, W. Zhu, J. Wang, C. Descorme, *Carbon* 46 (2008) 445–452.

[30] S. Yang, W. Zhu, X. Li, J. Wang, Y. Zhou, *Catal. Commun.* 8 (2007) 2059–2063.

[31] S. Yang, X. Wang, H. Yang, Y. Sun, Y. Liu, J. Hazard. Mater. 233 (2012) 18–24.

[32] R.S. Ruoff, D.C. Lorents, *Carbon Nanotubes*, Pergamon, in: M.E.I.S. Dresselhaus (Ed.), Oxford, 1996, pp. 143–148.

[33] G. Ovejero, J.L. Sotelo, M.D. Romero, A. Rodríguez, M.A. Ocaña, G. Rodríguez, J. García, *Ind. Eng. Chem. Res.* 45 (2006) 2206–2212.

[34] J. Restivo, R.P. Rocha, A.M.T. Silva, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo, *Chin. J. Catal.* 35 (2014) 896–905.

[35] J.P.S. Sousa, A.M.T. Silva, M.F.R. Pereira, J.L. Figueiredo, *Sep. Sci. Technol.* 45 (2010) 1546–1554.

[36] O.S.G.P. Soares, R.P. Rocha, A.G. Gonçalves, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira, *Carbon* 91 (2015) 114–121.

[37] O.S.G.P. Soares, R.P. Rocha, A.G. Gonçalves, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira, *Appl. Catal. B Environ.* 192 (2016) 296–303.

[38] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, F. Stüber, *Appl. Catal. B Environ.* 67 (2006) 12–23.

[39] F. Stüber, I. Polaert, H. Delmas, J. Font, A. Fortuny, A. Fabregat, *J. Chem. Technol. Biotechnol.* 76 (2001) 743–751.

[40] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, F. Stüber, *J. Chem. Technol. Biotechnol.* 80 (2005) 677–687.

[41] O.S.G.P. Soares, A.G. Gonçalves, J.J. Delgado, J.J.M. Órfão, M.F.R. Pereira, *Catal. Today* 249 (2015) 199–203.

[42] O.S.G.P. Soares, J.J.M. Órfão, M.F.R. Pereira, *Ind. Eng. Chem. Res.* 49 (2010) 7183–7192.

[43] C.E. Hori, H. Permana, K.Y.S. Ng, A. Brenner, K. More, K.M. Rahmoeller, D. Belton, *Appl. Catal. B Environ.* 16 (1998) 105–117.

[44] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, *Carbon* 37 (1999) 1379–1389.

[45] M.E. Suarez-Ojeda, J. Carrera, I.S. Metcalfe, J. Font, *Chem. Eng. J.* 144 (2008) 205–212.

[46] S.S. Lin, D.J. Chang, C.-H. Wang, C.C. Chen, *Water Res.* 37 (2003) 793–800.

[47] J.J. Delgado, X. Chen, J.A. Pérez-Omil, J.M. Rodríguez-Izquierdo, M.A. Cauqui, *Catal. Today* 180 (2012) 25–33.

[48] A. Santos, P. Yustos, A. Quintanilla, F. García-Ochoa, J.A. Casas, J.J. Rodríguez, *Environ. Sci. Technol.* 38 (2004) 133–138.

[49] Z.P.G. Masende, B.F.M. Kuster, K.J. Ptasinski, F.J.J.G. Janssen, J.H.Y. Katima, J.C. Schouten, *Top. Catal.* 33 (2016) 87–99.

[50] E. Pollak, G. Salitra, A. Soffer, D. Aurbach, *Carbon* 44 (2006) 3302–3307.